

# **Developments of Spent Nuclear Fuel Pyroprocessing Technology at Idaho National Laboratory**

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## **Abstract**

This paper summarizes research in used fuel pyroprocessing that has been published by Idaho National Laboratory over the last decade. It includes work done both on treatment of Experimental Breeder Reactor-II and development of advanced technology for potential scale-up and commercialization. Collaborations with universities and other laboratories are included in the cited work.

## **Introduction**

The Idaho National Laboratory (INL) has been active in the development of pyroprocessing technology since the 1980's. This includes work done at Argonne National Laboratory-West (ANL-West) up until 2005 when it was merged with the Idaho National Engineering and Environmental Laboratory to form the INL. Research and development in this area at INL has basically fallen under two missions—treatment of the spent fuel from the Experimental Breeder Reactor-II (EBR-II) and development of advanced technology to help close the nuclear fuel cycle and lead to commercialization.

## **Initial Focus on EBR-II Metal Fuel Treatment**

The development of pyroprocessing began in the 1980's at Argonne National Laboratory as an essential component of the Integral Fast Reactor (IFR) concept [1,2]. EBR-II was used as the test reactor for the IFR program, while the Fuel Cycle Facility (FCF) – now known as the Fuel Conditioning Facility – was equipped with pyroprocessing equipment to perform the fuel recycle functions of the IFR. The IFR program was terminated in 1994, but the fuel in the reactor core at the time was considered to be unsuitable for long-term geologic disposal without some form of stabilization. Pyroprocessing technology, sans the fuel fabrication step, was deemed as the most attractive option to achieve this stabilization. High-level waste components of the spent fuel are partitioned into ceramic and metallic waste forms suitable for permanent geologic disposal. Rather than collect Pu and other transuranic (TRU) elements for fabrication of new fast reactor fuel rods, those TRU elements could be partitioned into one or both of the waste forms. From 1996 through 1999, INL (ANL-West at the time) demonstrated the feasibility of pyroprocessing the EBR-II spent fuel by processing 0.4 MTHM of driver fuel, 0.7 MTHM of blanket fuel, and producing a limited number of ceramic and metallic waste form samples [3]. That demonstration was judged as successful by the U.S. Department of Energy, and pyroprocessing or electrometallurgical treatment was

designated as the preferred technology for treating the remaining inventory of spent EBR-II fuel [4].

In the 12 years since the completion of the EBR-II spent fuel treatment demonstration project, INL has continued to process spent fuel from EBR-II in addition to the Fast Flux Test Facility (FFTF). Table I shows the initial inventory of spent fuel and what has been processed to date. In this respect, processing includes fuel chopping, electrorefining, and cathode processing. There are two electrorefiners (ER) that have been used for processing the fuel, the Mark-IV ER and Mark-V ER. Each ER contains in excess of 500 kg of molten chloride salt containing actinides and active metal fission products (Group I, Group II, and lanthanides). Very little of this salt has yet been immobilized into ceramic waste forms, which is needed for long-term disposal. The original plan was to quickly transition from a demonstration project into production operations that would require 12 to 13 years to process the fuel. But the lack of sufficient funding to support production operations has substantially lengthened the time frame of the project. As can be seen in Table I, 74% of the EBR-II driver fuel and 86% of the EBR-II blanket fuel remains to be processed even though the original timeframe for complete treatment has elapsed. Essentially all of the FFTF driver fuel has been treated with a small amount set aside for fuel-related experiments. Currently, processing of EBR-II blanket fuel has been suspended with the processing focus on completing treatment of the driver fuel. It may be re-evaluated in the future whether to electrorefine the remaining blanket fuel inventory or to separate the sodium bond and dispose of that fuel without further treatment.

**Table I.** Inventory of Spent Fuel Designated for Pyroprocessing at INL.

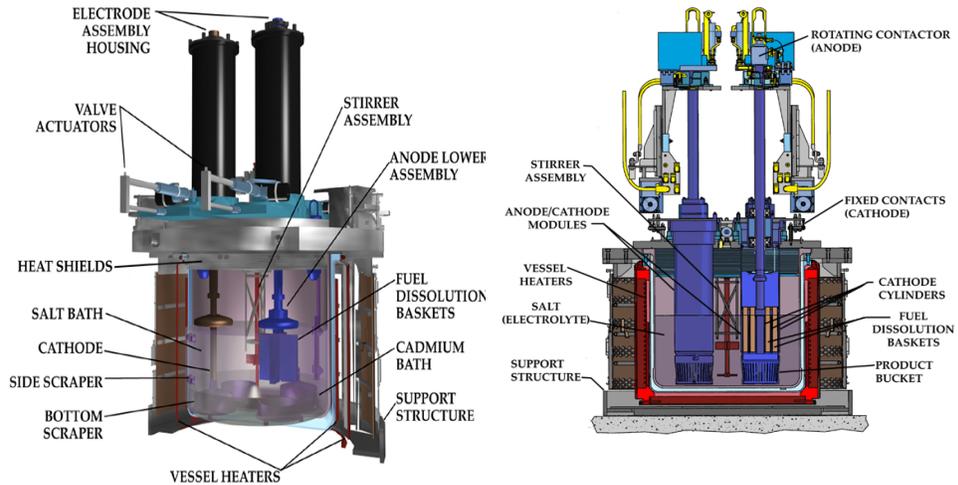
Fuel Type	EBR-II Driver (MTHM)	FFTF Driver (MTHM)	EBR-II Blanket (MTHM)	Total (MTHM)
Initial Fuel in June 1996	3.1	0.25	22.4	25.75
Fuel Treated as of January 2012	0.8	0.22	3.6	4.62
Remaining Untreated Fuel	2.3	0.03	18.8	21.13

The slower pace of production operations has allowed research and development on the spent fuel treatment process to continue. Most of the unit operations that comprise the spent fuel treatment process have received some attention in this regard. Highlights are listed below.

### *Electrorefining*

The electrorefiner (ER) is essentially the key unit operation in pyroprocessing. It is where the U is electrolytically separated from cladding hulls, bond sodium, and

noble metals in the spent fuel. There are two engineering scale ER systems at INL that are being used concurrently for treatment of spent EBR-II fuel. They are referred to as the Mark-IV and Mark-V ER. Figure 1 shows drawings of these systems, which occupy similar space in the Fuel Conditioning Facility (FCF) but have markedly different electrode designs.



**Figure 1.** Mark-IV (left) and Mark-V (right) Electrorefiners from the INL Fuel Conditioning Facility.

Numerous aspects of the Mark-IV ER have been studied and published during the treatment campaign to date in which approximately 830 kgHM of driver fuel has been electrorefined. Technical issues of interest have included current efficiency, U recovery efficiency, zirconium recovery, and understanding the interactions of the cadmium pool with the rest of the system [5-7].

Key goals of the electrorefining process are to dissolve as much of the U from the spent fuel as possible while retaining Zr and other noble metal fission products that by design should partition into the metal waste form. Li and Simpson studied the anodic dissolution process and analyzed the impact on U dissolution and noble metal retention [5]. It was concluded that diffusion of reactants in the porous fuel matrix was the rate-controlling step for the dissolution process. And there was found to be an inverse relationship between U dissolution and noble metal retention. Increasing the U dissolution to greater than about 98% resulted in significant loss of noble metals. This indicates that there is an optimal level of dissolution that can be controlled by the maximum anode potential. It was discovered that Zr dissolution could be completely eradicated by using an interrupting current technique [5]. Under the Advanced Fuel Cycle Initiative (AFCI) program, however, a stated goal was to achieve very high recycle efficiency for the actinides. Thus, a series of Mark-IV ER runs were performed with high anode

potentials in order to achieve near complete oxidation of the U. It was reported by Li that an average of 99.7% U dissolution could be achieved over several runs, but that came at the cost of very high (87.8%) loss of the Zr and moderate (23-27%) loss of the noble metal fission products [6]. In both cases, the losses are suspected to be from fine particles falling out of the basket and into the cadmium pool. The zirconium has been shown to accumulate in the Cd pool but can be recovered to a solid cathode via co-deposition of U/Zr. In this process, the Cd pool is anodically polarized. The resulting U/Zr deposit on a steel cathode has up to 22 wt% Zr [6].

During early operations of the Mark-IV ER, the current efficiency was approximately 50%. The inefficiencies are largely due to U dendrites falling off of the cathode into the Cd pool and then having to be re-electrorefined via a deposition cycle. A deposition cycle involves anodically polarizing the cadmium pool to promote electrotransport from the cadmium pool to the cathode. It was found that improving the agitation of the salt via rotating the anode baskets resulted in significant improvements in the efficiency to 65 to 76% [6].

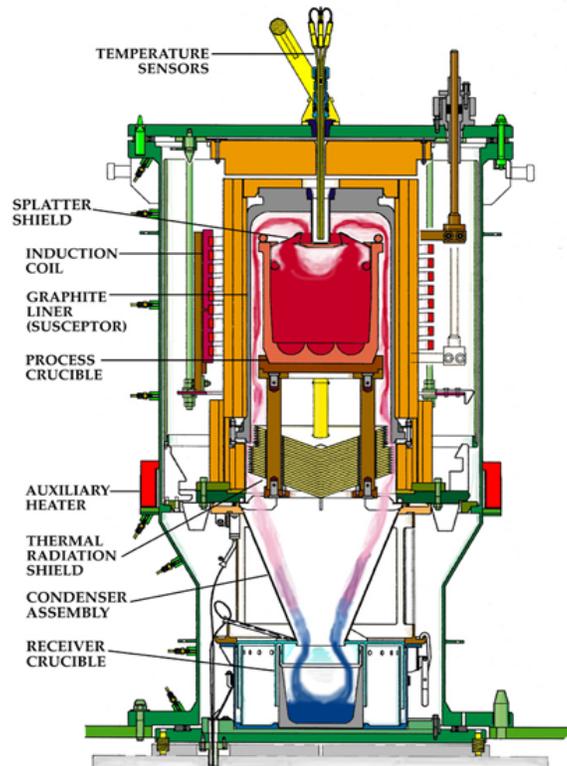
The cadmium pool is a unique feature of the Mark-IV ER. There is no such pool in the Mark-V ER. The motivation for including it in the system was largely to be used as a way of capturing U dendrites that fall off of the solid steel cathode mandrel. It was reported by Li, however, that the U also enters the Cd pool electrochemically [7]. It essentially acts as an intermediate electrode between the anode and cathode. U transports from the anode baskets to the nearby surface of the Cd pool. Simultaneously, U transports from the Cd pool to the nearby steel cathode. The concentration of U at any given time in the pool can be measured via the electric potential difference between the reference electrodes and the vessel which is in contact with the cadmium. The relation between potential and concentration was derived based on fundamental electrochemical principals and verified via comparison with experimental data. The pool is not without its drawbacks, however. The high vapor pressure of cadmium results in it condensing on various locations within the electrorefiner, which leads to electrical shorting in the ER vessel [7]. A Cd vapor trap was installed to mitigate this problem.

To enhance the understanding of fundamental chemical and physical processes that occur in the Mark-IV ER, a project was initiated in 2007 to develop a kinetic model of the ER [8-10]. This project was in collaboration with University of Idaho (UI), Seoul National University (SNU), and Korea Atomic Energy Research Institute (KAERI). It was officially a part of the US-ROK International Nuclear Energy Research Initiative (I-NERI) program. A team from UI developed a 2-D representation of the Mark-IV ER, while a team from Seoul National University developed a 3-D representation. Amongst other objectives, it was a comparative study of the importance of complexity versus computational economy for electrorefiner modeling. The model was able to track relative dissolution of uranium and zirconium throughout the process and agreed with experimental results in showing that to minimize the dissolution of Zr that the uranium dissolution must be limited [10]. A two-dimensional mapping of the electric

potentials in the Mark-IV ER revealed interesting insight into how to optimize the ER system design. It was shown that regions far from the operating electrodes have small potential gradients and little ion movement. Thus, it is advantageous to utilize all of the space inside of the ER with cathodes and anodes. Another insight gained from model development was that uranium concentration in the salt has a substantial affect on the electrorefining process [8]. Increasing the U concentration in the salt actually reduces the rate of U dissolution in the fuel and increases the rate of Zr dissolution. The model revealed the importance of the exchange current density physical property for accurately predicting electrorefining kinetics. Unfortunately, attempts to directly measure this parameter have yielded numbers inconsistent with fits of the electrorefiner model to process data [9,11].

### *Cathode Processing*

Uranium product from the electrorefiner is in dendritic form and is coated with chloride salt (typically 20 wt% of the product) from the ER electrolyte. After it has been harvested from the cathode mandrel (Mark-IV ER) or product collector (Mark-V ER), it is loaded into a crucible and inserted into the cathode processor (CP). In the CP, the temperature is raised to 1200°C under a vacuum ranging from atmospheric to 27 Pa. A drawing of the CP is shown in Figure 2.

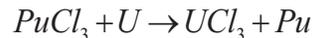


**Figure 2.** Cathode Processor Located in the INL Fuel Conditioning Facility.

Research related to the CP has been primarily focused on determining distillation efficiencies, minimizing U product contamination, and investigating different crucible options.

Distillation efficiency for active metal chlorides by design should be as close to 100% as possible. That is because these salts should be recycled to the electrorefiner or sent to the ceramic waste process. Over numerous runs during treatment of EBR-II driver fuel, it was found that the distillation efficiency for these active metals ranged from about 98.6 to 99.96% [12]. Interestingly, there was a linear correlation observed between mole fraction of any salt compound in the molten mixture and that compound's distillation efficiency.

As for the issue of product purity, the main objective is to ensure that the U product from blanket electrorefining is suitably pure so that it can be disposed of as a low level waste. Pu contamination, in particular, is an obstacle to such a waste management plan and has been observed routinely in the blanket U product. Experiments were performed that revealed the CP operation as the source of this Pu contamination [12]. In other words, the Pu is not initially in the metal deposit phase on the cathode. It goes into that phase during actual CP operations. As the salt is distilled, the following reaction becomes thermodynamically more favorable.

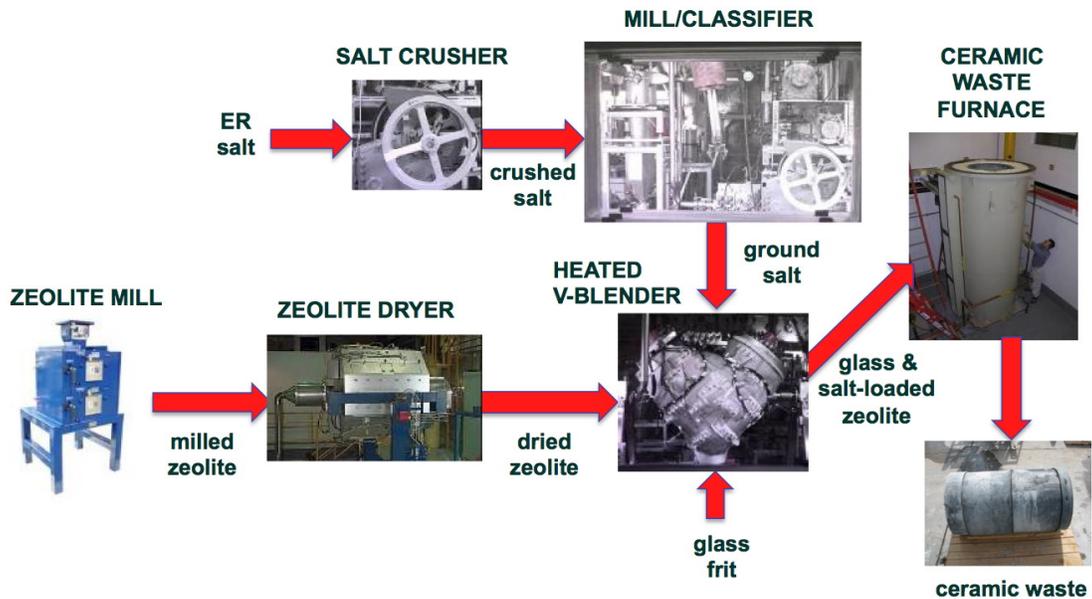


It was shown that Pu levels in the U product can be reduced by as much as 90% by adding cupric chloride to the salt, which effectively generates  $UCl_3$  and shifts the chemical equilibrium in the above equation to the left [12].

An investigation of different CP crucible materials was carried out. Initial operations utilized a graphite mold coated by a zirconia wash [12]. These crucibles are problematic with respect to the time required to clean and re-coat them. Also, the coating reacts with the salt/metal charge to form an oxide dross. Two alternative crucible materials have been investigated— castable zirconia and hafnium nitride coated niobium [12, 13]. The castable crucible also has the dross problem but significantly reduces the preparation time needed for each crucible and, thus, improves process throughput rate. The coated niobium crucible results in no dross formation and requires no preparation in between runs. But it will chemically react with any Zr in the cathode product. And it was found that the coating process developed more imperfections as the crucible size was increased to production scale (15 liters). The coated niobium crucible is also very expensive compared to the coated graphite and castable options. Thus, current production operations in the CP utilize the castable zirconia crucible.

## Ceramic Waste Processing

The reference process for preparing waste salt from the electrorefiners for permanent disposal is known as the ceramic waste process (CWP). The CWP consists of several unit operations, including zeolite size-reduction, zeolite drying, salt/zeolite blending, and pressureless consolidation [14-16]. Figure 3 shows a detailed flowsheet for the CWP featuring photographs of the engineering-scale equipment.



**Figure 3.** EBR-II Spent Fuel Treatment Ceramic Waste Process

The objective of the CWP is to immobilize the salt containing LiCl-KCl and active metal chlorides into glass-bonded sodalite ingots with a nominal mass of 400 kg. It has been estimated that at least 33 MT of ceramic waste forms will be needed to immobilize all of the salt that will eventually be generated from EBR-II SFT, corresponding to 82 waste forms of this size. Those waste estimates were based on a calculation that was performed in 2007 and may need to be updated based on current safety basis limitations in the INL hot cell facilities. Early development of this process used a hot isostatic press (HIP) for the final conversion of zeolite and glass powder into the waste form. But it was found that a higher temperature sintering process could achieve nearly the same result with only a slight decrease in density of the final waste form. The HIP process operated at a pressure of 25,000 psi and 850°C, while the pressureless consolidation (PC) process operates at atmospheric pressure and 925°C. Operation of a PC furnace in a hot cell was evaluated to be considerably more practical than utilizing a HIP. The weight of the equipment compared to the maximum load on the hot cell floor was a major issue of concern.

During initial stages of the development of the CWP, there was no standard established for dryness of the zeolite. Zeolite-4A, which has high aluminum content, is extremely hygroscopic and will quickly absorb greater than 20 wt% water into its pores. It was known that this water must be removed prior to blending with the salt to avoid a large release of steam in the closed V-blender. That steam would likely overpressurize the vessel and combine with the salt to cause widespread corrosion of the equipment. Furthermore, any residual water left in the zeolite could compete with the salt for absorption sites and, thus, reduce the capacity of the zeolite to immobilize salt. The approach taken with zeolite drying was to determine the level of dryness that could be practically obtained without overheating the zeolite or using an excessively long drying cycle. The moisture level that was selected as the process target was 0.3 wt% [16]. There are a variety of methods that can be used to analyze the moisture content in the zeolite, all of which require careful handling of the zeolite in a dry atmosphere to prevent re-absorption of water. The most reliable method was determined to be Karl-Fisher titration coupled with a tube furnace operating at 600°C [14,16]. Zeolite samples of approximately 10 mg are slid into the hot zone of the furnace with flowing dry gas. The gas carries any moisture thermally released into the titration cell. A custom dryer was developed to dry zeolite batches up to about 100 kg. This system, referred to as a Mechanically Fluidized Dryer (MFD) involves a retort that continually rotates inside of fixed heaters [14]. The motion of the retort does not effectively mix the zeolite powder but does promote heat and mass transfer via fluidization of the powder. Off-gas from the retort can either be released to the atmosphere or sent through a vacuum system. During initial heat up of the zeolite when most of the moisture is released, the steam is vented directly to the atmosphere. Once the temperature reaches 500°C, the system is sealed and off-gas is directed through a vacuum system. Drying tests performed in non-vacuum conditions indicated that the vacuum conditions result in lower residual moisture levels in the zeolite with all other conditions essentially the same. The standard heating cycle with the MFD system is to hold the zeolite at 500°C for 12 hours under vacuum. Moisture levels as low as 0.15 wt% have been obtained in this system under these conditions [16].

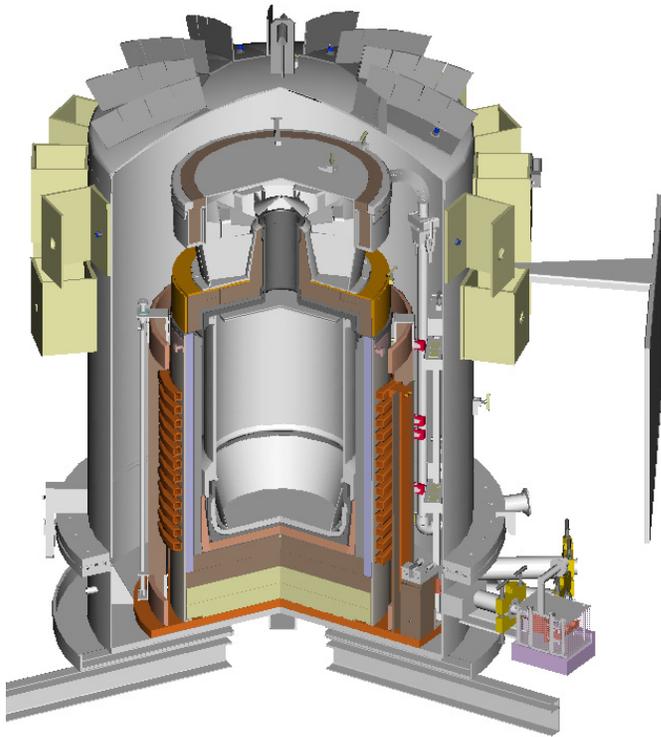
To immobilize the waste salt, it is blended with dehydrated zeolite-4A in a high temperature V-blender [14-16]. The V-blender is one of only three systems in the CWP that have been tested in a hot cell with real waste from used fuel. Unlike the MFD, its geometric design does facilitate powder mixing, which is important due to the need to distribute salt powder evenly through the batch of dried zeolite. With each rotation of the V-blender, the powder is divided into two volumes and then recombined. The off-set geometric design ensures that each rotation splits the powder differently. The operating conditions for the blending were established using both a laboratory-scale and an engineering-scale V-blender [15]. Free chloride measurements were used to quantify the effectiveness of each blending run. It was found that minimizing the amount of large particles in the milled salt is important for achieving a low free chloride value [15]. Holding the temperature at 500°C for 15 hours is typically sufficient to minimize the free chloride. Frequently, it was observed that salt/zeolite cakes on some regions of the inner V-blender wall.

Strategies have been proposed to minimize this caking but have not yet been tested. Final optimization of the V-blender process should address this caking issue, which has been observed in both laboratory-scale and engineering-scale V-blender experiments.

Recent developments in pressureless consolidation have been attained via full-scale testing with surrogate salts [16]. A multi-section container was designed, built, and tested to contain the ceramic material during consolidation. The volume is reduced approximately 60% as a result of consolidation, leaving much excess length in the container that would otherwise need to be cut off and discarded. The design of the multi-section container is such that the upper half is removed after consolidation and then used as the lower half of the next container. For the 400-kg sized waste forms, the temperature cycle involves a 40-hr hold at 500°C followed by a 75-hr hold at 925°C [16]. A forced cool-down can minimize the overall cycle time, but it has been found that cracking of the ceramic occurs during this cooldown. During one full-scale waste form run, 14 cracking events were detected using a microphone placed outside of the furnace and audio recording software. Solidification stress is believed to be the cause of the cracking, not thermal stress. Solidification stress theory and its comparison to the pressureless consolidation data was presented by Solbrig et al. [17].

### *Metal Waste Processing*

After each fuel batch is electrorefined, the cladding hulls remain in the anode baskets along with unreacted actinides, zirconium, and noble metals. It has been shown that zirconium and noble metal retention is a function of the extent of actinide removal [5]. But most of these elements tend to be retained with the cladding hulls. When the anode baskets are pulled from the salt, a significant coating of salt remains on the surface of the hulls. This salt is separated via distillation in the metal waste furnace, which is pictured in Figure 4. The metal waste furnace also serves to consolidate the cladding hulls and residual fuel constituents into a metallic ingot that is suitable to be disposed of as a high level waste form.



**Figure 4.** Metal waste furnace designed to process cladding hulls from the electrorefining of spent EBR-II fuel.

In addition to cladding hulls, plenums containing sodium metal are also processed in the metal waste furnace [18]. Iron chloride is added to the process crucible and heated to 800°C for 75 min to convert the sodium to sodium chloride. Salt distillation and melting of the metal alloy ingot is accomplished via heating the process crucible to 1560°C for 3 hrs under vacuum. The metal waste furnace is inductively heated and capable of reaching 1700°C under a vacuum of 200 mTorr.

Zirconium is added to the process crucible in the form of 1.5 mm diameter wire [18]. This is necessary to bring the metal waste form composition to a target value of 15 wt% zirconium with a minimum of 5 wt% and maximum of 20 wt%. The metal waste form is primarily composed of two metallographic phases, a ferrite solid solution, and a FeZr<sub>2</sub>-type intermetallic. Actinides are exclusively bound in the FeZr<sub>2</sub> intermetallic. The noble metal fission products are also found in the intermetallic, though cobalt, molybdenum, manganese, tin, and technetium also have some solubility in the ferrite solid solution. Zirconium contents less than 5 wt% are unable to encapsulate fission products and actinides [19-22]. Alloys with greater than 20 wt% zirconium have increased brittleness.

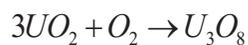
Crucible material selection was found to be key due to the high reactivity of uranium trichloride in the salt with some oxides and the reactivity of sodium metal with graphite. An alumina refractory lined graphite was selected with the plenums placed inside of a thin-walled steel liner to prevent sodium metal reaction with graphite [18]. The sodium is oxidized to sodium chloride via reaction with iron chloride during the metal waste furnace run.

### **Conditioning Oxide Fuel for Pyroprocessing Treatment**

While the U.S. Department of Energy currently envisions pyroprocessing as being ideally used for recycle of metallic fast reactor fuel, research at INL has been performed in support of light water reactor (LWR) oxide fuel conditioning to make it compatible with electrorefining. In recent years, this has been primarily motivated via collaboration with the ROK under the International Nuclear Energy Research Initiative (I-NERI) program and more recently the US-ROK Joint Fuel Cycle Study (JFCS) program.

#### *Voloxidation*

Voloxidation is the high temperature process by which oxygen or air reacts with oxide spent fuel. The primary oxidation reaction is as follows.

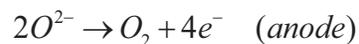
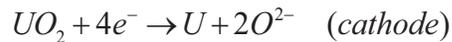


This can be the head-end step for either pyroprocessing or aqueous processing of spent fuel. Benefits to its use include removal of volatile fission products, separation of fuel from cladding, and particle size reduction to promote fast reaction kinetics for the oxide reduction process or fast dissolution rates for aqueous processing. INL collaborated with KAERI and Oak Ridge National Laboratory (ORNL) on development of this process. In 2008, results of voloxidation tests using spent BR-3 fuel with different process parameters were summarized [23]. Oxidation temperatures ranged from 500 to 700°C. Effect of vacuum at high temperature (950°C) after lower temperature oxidation was examined. The effect of air versus O<sub>2</sub> as the oxidant was examined. And the effect of cladding versus no cladding was examined on removal of various fission products. Analyses included particle size, percent fuel removal from the cladding, and removal of various fission products. Six fission products were found to be significantly depleted from the fuel due to the voloxidation experiments—including rhodium, ruthenium, technetium, molybdenum, tellurium, and cesium. Complete removal of the fuel from the cladding was achieved with an oxidation temperature of only 500°C for 2 hours. Increasing the temperature, however, resulted in less fines in the oxidized powder product. Increasing the oxidation temperature also tended to increase the removal of fission products. Applying vacuum at 950°C after the fuel oxidation was also found to assist in the removal of fission products.

An off-gas treatment system (OTS) has been developed with the objective to trap key volatile fission products—iodine, technetium, and cesium [24]. The OTS consists of three zones, each containing a different solid absorbent and maintained at a different temperature. Zone 1 contained AgX zeolite and was held at 150°C with the objective of collecting the iodine. Zone 2 contained CaO/fly-ash (Si/Al=2) at 600°C for collecting technetium. Zone 3 contained fly-ash at 1000°C and was used for collecting cesium. Three samples of spent fuel were run in the four-zone voloxidation system with oxidation of the fuel at 500°C. After an initial run in which incomplete fuel oxidation was observed, the next two runs yielded data that demonstrated the effectiveness of these filters. The iodine trapping was particularly efficient with 84 to 100% collection based on initial iodine content in the fuel estimated using ORIGEN. Optimal technetium collection of 72% was observed in Zone 2 based on initial technetium concentration determined via fuel sampling. And up to 66% of the cesium was found to collect in Zone 3—also based on sampling of the initial fuel. The only unexpected result was the detection of equimolar concentrations of cesium and technetium in the tubing connecting the zones. This has been hypothesized to be due to the formation of CsTcO<sub>4</sub>.

### *Oxide Reduction*

Whether oxide fuel is first voloxidized or not, it must be reduced completely to metallic form prior to processing in an electrorefiner. While early research into an oxide reduction process focused on chemical reduction using lithium metal dissolved in LiCl [25], focus in the last decade has been on electrolytic reduction using LiCl-Li<sub>2</sub>O as the electrolyte. The reactions at each electrode are listed below.



The electrolytic reactions keep the lithium oxide concentration from increasing and simplifies the process to only a single furnace and vessel.

All electrolytic reduction experiments performed at INL have involved lab-scale molten salt furnaces with maximum fuel batches of about 50 grams. Experiments with spent fuel were performed in the Hot Fuel Dissolution Apparatus (HFDA), a lab-scale molten salt furnace installed in the Hot Fuel Examination Facility (HFEF) hot cell. The fuel was either mechanically crushed [26] or voloxidized [27] to achieve small particles prior to loading in the cathode baskets. Spent fuel samples used in these studies included fuel from the Belgian light water reactor, BR-3 [26, 27, 31] and MOX fuel that had been irradiated in EBR-II [32].

In studies with used BR-3 fuel, current efficiency was observed to vary from 21 to 45% [26]. Fission products cesium, barium, strontium, and iodine partitioned into the salt phase with very low concentrations of uranium and plutonium detected. Up to 99.7% reduction of UO<sub>2</sub> to U metal and 97.8% reduction of PuO<sub>2</sub> to Pu metal was

observed [26]. Meanwhile, rare earth reduction was less with an upper value of about 80%. In some cases, batches of BR-3 fuel that had been electrolytically reduced were then subjected to electrorefining [31]. In these runs, no effort was made to remove the adhering salt from the oxide reduction process. Uranium metal deposits were successfully obtained, and rare earth fission products were found to accumulate in the LiCl-KCl salt as expected. There were some interface issues discovered between the oxide reduction and electrorefining steps. Salt carryover resulted in higher than normal depletion of uranium from the salt, in part from reaction with lithium oxide to make uranium oxide.

In addition to reducing crushed BR-3 fuel, some batches of this fuel were first dechlorinated via voloxidation, which resulted in particle size reduction and loss of volatile fission products. The voloxidized fuel has a chemical state of  $U_3O_8$ , which was found to readily convert to U metal in the oxide reduction process [27]. Voloxidation results in a fraction of the fuel having a particle size of less than 45  $\mu\text{m}$ , and those particles were separated from the rest of the material via sieving prior to running in the oxide reduction process. Either sintered metal or porous magnesia baskets were used to contain fine fuel particles.

MOX fuel that had been irradiated in EBR-II was also used in oxide reduction tests [32]. A wide range of reduction efficiencies were observed with the MOX fuel, but the efficiency appeared to improve with each of the five runs completed. This appeared to be partially due to varying levels of unintentional re-oxidation of samples during storage. Elevated concentrations of iodine and tellurium were observed in the salt from reducing MOX fuel, and that appeared to lead to significant chemical attack on the platinum anode. Examination of the anode after testing indicated about 20% loss of the platinum. Anode potentials progressively increased during the MOX fuel treatment, significantly more than had been observed with LWR fuel treatment. Electrorefining was also performed on the reduced MOX fuel. This resulted in higher than normal concentrations of TRU in the solid cathode deposits (1.7 to 15%), which may be attributed to a drop in  $UCl_3$  concentration in the salt from reaction with the TRU elements. One liquid cadmium cathode run was performed for the purpose of U/TRU recovery that resulted in a Pu/U ratio of 4.2 in the metal deposit.

Some kinetic testing and modeling have also been done on oxide reduction as part of a collaboration with KAERI. In an International Nuclear Energy Research Initiative (I-NERI) project, a series of laboratory-scale uranium oxide samples were reduced in a molten salt furnace installed in an inert atmosphere glove box at INL [28]. Additional data was collected at KAERI in their laboratory-scale systems [30]. These experiments involved runs with both stainless steel mesh and sintered stainless steel baskets in an attempt to understand the effect of the basket on the kinetics. Higher retention of lithium oxide was measured in the sintered stainless steel baskets, indicating that diffusion of the lithium oxide out of the fuel was effectively restricted with the sintered metal baskets. Partial reduction tests were attempted to obtain data useful for kinetic modeling. Much of the data was suspect, however,

as there was not always a consistent relationship between applied charge and extent of reduction. The kinetic model developed by University of Idaho for oxide reduction was focused on the processes occurring at the cathode and assumed the kinetics were limited by charge transfer and diffusion [29]. Validation of the model was hindered by the inconsistent kinetic data.

### *Oxide Reduction Salt Treatment*

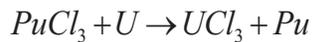
One of the technical challenges associated with development of an oxide reduction process is how to manage the waste salt generated. The molten LiCl-Li<sub>2</sub>O electrolyte, as previously discussed, is contaminated by a number of fission products including cesium, strontium, barium, and iodine [26]. Concentration limits have not yet been established for these elements in the salt, but it is certain that they will have to be regulated. The negative impact of fission product accumulation was observed during the previously mentioned reduction of irradiated MOX fuel [32]. One option is to carryover salt from oxide reduction to electrorefining and replace the salt with clean LiCl-Li<sub>2</sub>O. This would result in significant conversion of UCl<sub>3</sub> in the salt to UO<sub>2</sub> from reaction with the lithium oxide, and that UO<sub>2</sub> would need to be collected and recycled to the oxide reduction step. Alternatively, the salt can be distilled off of the reduced fuel and recycled to the oxide reduction system. That leaves two options for dealing with fission product accumulation—throw-away of the salt (as in the ceramic waste process) or selective chemical separation. The latter option was investigated by Sachdev et. al. [33]. In this study, the ability of zeolite-4A to selectively absorb or exchange Cs<sup>+</sup> and Sr<sup>2+</sup> cations out of LiCl was examined. Both molten salt and solidified powder salt were studied. The molten salt contacts were done at 650°C, and it was found that the zeolite degraded at that temperature and was ineffective at removing the fission products from the salt. The solid state contact tests with the powders were done in a small scale V-blender at 500 and 550°C. In those tests, the zeolite retained its crystalline structure and removed as much as 99.6% of the Cs and 99.5% of the Sr from the salt. This solid state ion exchange process with zeolite-4A, thus has potential for cleaning up the oxide reduction salt.

### **Technology Development to Support Commercialization of Pyroprocessing**

Key objectives to commercializing pyroprocessing are recovering actinides for recycle to new fuel and minimizing the volume of high level waste generated by the process. The latter issue is largely contingent upon effectively handling the contaminated salt from the electrorefiner. The ceramic waste process previously mentioned is effective at immobilizing the ER salt into a robust waste form. However, it is non-selective in nature and involves the loss of useful LiCl, KCl, and actinides from the process. Thus, research in recent years has been funded at INL to examine both actinide recovery and salt waste minimization. This technology is not intended to be applied to the processing of used fuel from EBR-II. Rather, it is to support future application of the technology in scaled up and perhaps commercialized installations.

### *Actinide Recovery*

While standard electrorefining onto a steel cathode typically results in a high purity uranium metal and very little co-deposition of transuranic (TRU) elements, a liquid cadmium cathode (LCC) has been shown to be effective at simultaneously collecting both U and TRU elements [34]. The LCC is effective due to the stabilization of plutonium metal in the cadmium phase. It has a very low activity coefficient in the cadmium phase compared to uranium, which shifts the equilibrium for the following reaction to the right.



Without the cadmium phase present, the reaction proceeds in the opposite direction and results in oxidation of any plutonium metal back into the salt phase.

INL has performed a number of LCC experiments using both the engineering-scale Mark-V ER and the lab-scale HFDA [35-38]. Engineering scale tests were reported by Vaden et. al. [35]. In these tests, 26 kg of cadmium metal was loaded into a beryllium oxide crucible and lowered into the salt. Three tests were performed, each resulting in 1-2 kg of heavy metal collected. The Pu/U ratio in the salt was initially 10.8 but dropped to 3.7 as a result of the LCC tests. With decreasing Pu/U in the salt, the Pu/U in the LCC product also decreased. Current efficiency was found to range from 76-99% with dendrite formation being a probable source of inefficiency. A pounder was used to minimize formation of these dendrites but was only successful in one of the three runs. Technically, it was a paddle that rotated and oscillated up and down during the experiments. Its range of motion extended to just above the cadmium surface to avoid displacement of cadmium from the crucible. The beryllium oxide crucibles were found to be easily damaged and, thus, do not appear to be a viable option for long term, reusable crucibles.

One of the primary objectives of running laboratory-scale LCC tests was to collect data to support calculation of separation factors of both actinides and rare earths between the salt and cadmium phases. In the engineering scale LCC tests, separation factors for rare earths could not be calculated due to the fact that they are present in very low concentrations in the Mark-V ER. In the laboratory-scale HFDA system, it is possible to spike rare earth chlorides into the salt to run tests capable of generating such separation factors. Li et. al. reported two series of experiments, one with equilibrium conditions and one with non-equilibrium conditions [36, 37]. In one set of tests, Mark-IV salt with 2 wt% rare earths was used. In the other set of tests, rare earths were spiked into a mixture of Mark-IV and Mark-V salt to a level of 5 wt%. In the equilibrium tests, the LCC was allowed to sit in the salt for a period of time after the electric potential was shut off. In the non-equilibrium tests, the cathodes were immediately pulled out of the salt after the potential was shut off. Over both series of experiments, the Pu/U ratio in the salt

varied from 0.8 up to 3.6. Plutonium recovery was measured over this entire range, but the ratio of Pu/U in the LCC product was found to be a linear function of the ratio in the salt. Rare earth contamination in the LCC product was measured to be as high as 6.7 wt%. Separation factors were measured for rare earths, and they were found to be strongly dependent on the cathode potential; i.e., the more cathodic the potential, the higher concentration of rare earths in the LCC [37]. Cathode potential did not have a significant effect on minor actinide separation factors, which has a benefit with respect to proliferation. A detailed analysis of the lab-scale LCC test results was published in 2010 [38]. Measured separation factors relative to U were shown to be smaller than published in the literature. And it was concluded that an LCC should be operated as close to its open circuit potential as possible to minimize rare earth contamination. It was recommended to use an LCC with a large surface to volume ratio which would then minimize the current density at the interface and make the cathode potential less negative.

Another approach to recovering actinides from electrorefiner salt is referred to as drawdown. Drawdown can be an electrochemical or chemical process that extracts U and TRU from the salt. Unlike the LCC electrorefining process, it can be used to achieve very low concentrations of actinides in the salt. At INL, drawdown using lithium reduction has been investigated [39]. In this work to date, rare earth chlorides have been used as surrogates for actinide chlorides. The objective of the experiments has been to understand the selectivity of drawdown using lithium as a function of thermodynamic properties. To understand how well actinides may be removed from the salt while leaving rare earths unreduced, rare earth pairs with different free energy of formation values were reacted with lithium. Given free energy differences comparable to those between actinides and rare earths, it was found that there is relatively poor selectivity. Using lithium to reduce a large fraction of the plutonium chloride from the salt is expected to also result in substantial reduction of rare earths. Thus, other drawdown methods are currently being investigated.

### *Salt Waste Minimization*

In order to minimize the generation of salt-related waste from pyroprocessing, research emphasis has been focused on selectively removing fission products from the LiCl-KCl salt. The most thoroughly investigated technology for this purpose is salt-zeolite ion exchange. In this process, ions from the molten salt replace ions initially in the zeolite. If the zeolite is pre-loaded with Li<sup>+</sup> or K<sup>+</sup> ions, the effective outcome is to cleanup the salt from the ER. Early investigation of this process by researchers at ANL showed that there was favorable selectivity for fission products in the zeolite [40]. This motivated a series of experimental studies in which molten salt solutions were contacted with dehydrated zeolite-4A for 24 hrs or longer to achieve ion exchange equilibrium [41-43]. Each fission product was investigated separately by preparing chloride salt mixtures containing LiCl, KCl, and a select fission product chloride. By this approach, it was possible to develop uptake curves as a function of final concentration in the salt. And this led to the development of

equilibrium models. The first model proposed by INL was based on the concept that there are two active sites for exchange in the zeolite—framework sites and occluded sites [43]. The framework sites are where cations balance the negative charge of the Al-O tetrahedra. Initially, zeolite-4A contains Na<sup>+</sup> cations to serve this purpose. The other site originates from the diffusion of salt molecules into the zeolite pores. Approximately 12 Cl<sup>-</sup> ions can absorb into the zeolite per pseudo unit cell based on the following formula where M is a generic metal cation with a +1 charge. The M<sup>+</sup> cations are effectively the second site for ion exchange, as they can be replaced by fission product cations from the salt.



Phongikaroon et. al. later expanded the model to include divalent and trivalent fission products with data to support fitting of the model [44]. The most recent work on the ion exchange model included the ability to predict the moles of salt occlusion per unit cell of the zeolite and expanded the data fit to include more experimental data [45]. The fission products that are now included in the fully predictive equilibrium model include Cs<sup>+</sup>, Rb<sup>+</sup>, Sr<sup>2+</sup>, Nd<sup>3+</sup>, Ce<sup>3+</sup>, Ba<sup>2+</sup>, La<sup>3+</sup>, Pr<sup>3+</sup>, and Y<sup>3+</sup>. U<sup>3+</sup> is also included in the model as well as the base salt components (Li<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup>).

Most recently, study of salt-zeolite ion exchange has expanded into kinetic investigations. Equilibrium is typically achieved in 24-72 hours, but that might be considered too long for a scaled up, commercial process. Shaltry et. al. used ternary and quaternary salt experiments, similar to those used for the equilibrium tests, with focus on rate of uptake of Cs<sup>+</sup> and Sr<sup>2+</sup> [46]. A novel experimental method was introduced in this study to maximize the useful data from each experiment. The volume of salt to volume of zeolite was high enough that the salt composition did not change significantly during each test. But the zeolite composition did change substantially with uptake of the Cs or Sr. To obtain kinetic data over a wide time range with each experiment, a few pellets of zeolite were removed every hour or two followed by re-immersion of the basket into the salt. Then each set of pellets were washed, dissolved, and analyzed to determine uptake of the fission product of interest at the time of the sample. Several models were considered with the best fit to a diffusion-limited model. Time to complete exchange was about 30 minutes for Cs and 100 min for Sr, but that was using a standard bead size of 2-mm diameter. Based on the conclusion that the exchange was diffusion limited in the beads, smaller particles should result in faster uptake of the fission products. Allensworth combined molten salt contacts and solid-state powder contacts to investigate the mechanism of salt transport into the zeolite particles [47]. It was shown in this study that a molten state for the salt is not required to achieve absorption of the fission products into the zeolite. This opens the door for different approaches to removing fission products from molten salts, especially for salt systems such as LiCl-Li<sub>2</sub>O that have very high melting points. It also shows that it is possible to absorb concentrated fission products into the zeolite after LiCl-KCl has been separated and recycled to the ER. This is important for connecting the zeolite-based ceramic waste

process to a zone freezing method (which selectively removes LiCl-KCl from the salt) for minimizing salt waste from the ER.

## Conclusions

Over the last decade, Idaho National Laboratory has been a leader in the development of pyroprocessing technology in the United States via processing of Experimental Breeder Reactor-II fuel and study of advanced technology to support potential scale-up of the process. In the process of treating 16% of the original inventory of EBR-II fuel, much has been learned about pyroprocessing at INL. Advancements have been made in electrorefining, cathode processing, and waste processing as a direct result of the EBR-II fuel treatment project. Tremendous amounts of data have been collected, and models for various unit operations have been developed and validated against data. While the technology was originally developed for metal fuel such as EBR-II driver and blanket fuel, significant progress has been made toward developing the unit operations needed to efficiently treat oxide fuel using pyroprocessing and to recover actinides for application to a closed nuclear fuel cycle. Key current challenges for process development include achieving high efficiency for actinide recovery, minimizing high-level waste generated by the process, and demonstrating the ability to effectively safeguard nuclear materials in a pyroprocessing facility. Work continues on these challenges, utilizing the INL's unique processing facilities and expertise while leveraging partnerships with other laboratories and universities.

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